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CLEANING OF HARD SURFACE

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INVENTOR(s): SHINDO AKINORI
APPLICANT(s): HOYA CORP [330074] (A Japanese Company or Corporation), JP
(Japan)
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ABSTRACT

PURPOSE: To prevent the occurrence of new contamination by a method wherein ultraviolet light is irradiated on the hard surface, whereon organic foreign substances exist, of a matter to be cleansed before the matter to be cleansed is cleansed with a cleaning fluid.

CONSTITUTION: In case the hard surface, whereon organic foreign substances exist, of a matter to be cleansed is dried after being cleansed with a cleaning fluid, ultraviolet light is irradiated on the hard surface before the cleaning. That is, by irradiating the ultraviolet light on the matter to be cleansed before the matter to be cleansed is cleansed with the cleaning fluid, the organic foreign substances of a photo resist and so on remaining on the surface of the matter to be cleansed are subjected to chemical change, are decomposed and disappeared on the spot and are brought in a state that they are easy to dissolve or peel with the cleaning fluid in a cleaning treatment to be executed with a cleaning fluid subsequent to that. Thereby, it is eliminated that organic foreign substances remain on the surface of the matter to be cleansed after the matter to be cleansed is subjected to cleaning treatment with a cleaning fluid and the occurrence of new contamination can be prevented.

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⑮ 発明の名称 硬表面の洗浄方法

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⑱ 発 明 者	進 藤 昭 則	東京都新宿区中落合2丁目7番5号 ホーヤ株式会社内
⑲ 出 願 人	ホーヤ株式会社	東京都新宿区中落合2丁目7番5号
⑳ 代 理 人	弁理士 中村 静男	

明 細 書

1. 発明の名称

硬表面の洗浄方法

2. 特許請求の範囲

有機系異物が存在する硬表面を洗浄液により洗浄した後に乾燥する洗浄方法において、前記洗浄液による洗浄の任意の工程の前に前記硬表面に紫外線を照射する工程を設けたことを特徴とする硬表面の洗浄方法。

3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は硬表面の洗浄方法に係り、詳しくは、例えば半導体プロセスにおいてフォトリソグラフィやフォトリソ、あるいは半導体基板等を洗浄する場合に用いられる湿式洗浄方法に関する。

〔従来の技術〕

従来この種の湿式洗浄方法としては、一般に、被洗浄物を少なくとも2種以上の洗浄液（例えば硫酸、純水、アルコール等）に順次浸漬し、必要に応じて洗浄液中に超音波を伝達させて洗浄処理

した後、アルコール等の蒸気により洗浄液を気化し乾燥する方法が知られている。

〔発明が解決しようとする課題〕

しかしながら、上記した湿式洗浄方法により被洗浄物を洗浄処理した場合、洗浄処理したにもかかわらず、洗浄処理後の被洗浄物に汚れの存在が認められる。その原因として、被洗浄物上に固着している残留レジスト等の有機系異物が上記洗浄処理によって完全には除去されずに洗浄処理後も被洗浄物上に一部残留することが挙げられる。また他の原因として、被洗浄物上に固着している残留レジスト等の有機系異物が洗浄処理に用いられる有機溶剤等の洗浄液と化学反応して被洗浄物の表面に新たな反応生成物として沈着することが挙げられる。さらにもう1つの原因として、洗浄処理において用いられる異なる種類の洗浄液の化学反応により、被洗浄物の表面に新たな反応生成物が生じることが挙げられる。この異なる種類の洗浄液間の化学反応による汚れの発生について更に具体的に述べると、この種の被洗浄物の洗浄処理には、

例えば硫酸浸漬洗浄とアルコール浸漬洗浄とを組み合わせた洗浄処理が採用されているが、この洗浄処理において、硫酸浸漬洗浄後、アルコール浸漬洗浄前に純水3相による浸漬洗浄が行なわれるが、このような純水洗浄処理を介在させたとしても被洗浄物の表面上に異物等が存在したり、被洗浄物の表面ぬれ性が不均一である場合には、純水洗浄処理後に硫酸が被洗浄物表面に付着残留し、これが次のアルコール浸漬洗浄処理時にアルコールと反応して一種のエステル化反応生成物を生じる。そしてこの場合の反応生成物に起因する汚れは再び硫酸やアルコール等の洗浄液により洗浄処理しても除去することが困難で、特に厄介なものである。

上述の如く従来の露式洗浄方法では、被洗浄物の表面に因着している有機系異物からなる汚れを完全に除去することは困難であり、この有機系異物と洗浄液との反応、洗浄液同士の反応により新たな汚れが被洗浄物の表面に発生するという問題点があった。

物が残留することがない。

また紫外線照射処理によって前記の有機系異物は洗浄液による洗浄処理時に被洗浄物の表面上に最早存在していないので、有機系異物と洗浄液との化学反応により新たな反応生成物が被洗浄物表面上に形成し残ることもない。

さらに紫外線照射処理によって被洗浄物の表面ぬれ性が改善されるので、洗浄液が被洗浄物表面に均一に行き渡り、洗浄液による洗浄処理を被洗浄物全体に均等に行なうことができるばかりでなく、被洗浄物を洗浄液から引き上げた時に水切れが容易であり、洗浄液が被洗浄物の表面の一部に集中的に残留することがなくなるので、例えば硫酸浸漬洗浄処理とアルコール浸漬洗浄処理とを組み合わせた洗浄方法において、前段の硫酸処理と後段のアルコール処理との間に、被洗浄物表面にわずかに残留する硫酸を除去するための微量な純水浸漬洗浄処理を設ければ、硫酸とアルコールとの化学反応による新たな汚れの発生も起らない。

【実施例】

本発明は、このような問題点を解決するためになされたものであり、その目的は、被洗浄物の表面に因着した有機系異物からなる汚れを完全に除去し引くと共に洗浄処理に伴う新たな汚れの発生のない洗浄方法を提供することにある。

【問題点を解決するための手段】

本発明は、上記目的を達成させるためになされたものであり、有機系異物が存在する被表面を洗浄液により洗浄した後に乾燥する洗浄方法において、前記洗浄液による洗浄の任意の工程の前に前記被表面に紫外線を照射する工程を設けたことを特徴とするものである。

【作用】

洗浄液による洗浄前に被洗浄物に紫外線を照射することにより、被洗浄物の表面に残留しているフォトリソ等の有機系異物が化学変化を受け、その場で分解消失したり、その後の洗浄液による洗浄処理において洗浄液によって溶解又は剥離しやすい状態になるので、被洗浄物の洗浄液による洗浄処理後に被洗浄物の表面上に前記の有機系異

被洗浄物の硫酸洗浄、純水洗浄及びイソプロピルアルコール（以下IPAと略称する）洗浄を順次行なった後、被洗浄物をIPA蒸気を用いて乾燥する従来のフォトリソ洗浄方法において、硫酸洗浄前に被洗浄物を紫外線照射処理する実施例について以下に説明する。

被洗浄物として、周知のレジスト工程、エッチング工程およびフォトリソ剥離工程を経て得られたフォトリソを用いた。すなわち、被洗浄物であるフォトリソは、透光性ガラス基板上にクロム透光性膜を被覆してなるフォトリソブランク上にポジ型フォトリソであるAZ-1350（ヘキスト社製）を塗布し、所望パターンを有するマスクを介して露光、現像した後、レジストパターンをマスクとして透光性膜をエッチングし、さらにレジストパターンを剥離したものである。

このフォトリソ（大きさ5×5×0.09インチ）4枚を、低圧水銀灯を具備してなる紫外線照射装置（処理室容積：3240cm³）内に配置

し、紫外線照射処理を行なった。

処理条件は、以下の通りである。

紫外線照度…2537Åの輝度の強度が全体の90%、1849Åの輝度の強度が全体の数%である低圧水銀灯を用いた。

低圧水銀灯に供給する総パワー…770W

ウェットエア…紫外線照射装置のガス導入口から30ℓ/分の流量で導入した。ウェットエアは紫外線照射時にO₃の発生効率を向上させる作用をする。

処理時間…5分

紫外線照射処理後の被洗浄物を次いで洗浄処理し、乾燥処理した。すなわち、洗浄処理は、被洗浄物を濃度98%の過硫酸1槽に5分間浸漬し、次に純水1槽に30秒間浸漬し、更にIPA1槽に3分間浸漬することにより行なった。なお被洗浄物のIPA槽浸漬に際しては、IPA液中に超音波(45kHzと46kHzの周波数を交互に繰

り返し発生する発振器を使用した。パワーは400Wである。)を伝達して超音波洗浄を行なった。

前記洗浄処理後の乾燥処理はIPA槽から引き上げられた被洗浄物をIPA蒸気中に浸漬することにより行なった。

上記の如く紫外線照射処理後に洗浄、乾燥処理された被洗浄物16枚について、その汚染化の割合を調査したが、16枚ともに汚れが認められなかった。

なお、紫外線照射処理を行わずに同様の洗浄、乾燥処理を行なった被洗浄物15枚についても同様にその汚染化の割合を調査したが、15枚ともに全面に汚れが認められた。また洗浄処理において純水浸漬洗浄処理を3槽とし、各槽浸漬時間をそれぞれ100秒としても、紫外線を照射しない場合には被洗浄物の全面に汚れが認められることが多々あった。

この実施例の結果から、紫外線照射処理を行なう本発明の方法によれば、被洗浄物表面上に固着している有機系異物が効果的に除去されており、

かつ洗浄処理時の化学反応に伴う新たな反応生成物の発生もないので、洗浄処理後の被洗浄物の汚染性が十分に確保されることが明らかである。

上の実施例では被洗浄物として、ポジ型(光分解型)フォトレジストが残留固着しているフォトマスクを用いたが、本発明の方法においてはネガ型(光硬化型)フォトレジストが残留固着している被洗浄物を洗浄処理することもでき、またレジストがポジ型及びネガ型電子線レジストであっても同様である。

また本発明の方法は、フォトマスクの洗浄に限定されるものではなく、フォトマスクブランク、ガラス基板、透明導電膜付きガラス基板、シリコンウエハ等、更にはカメラレンズ等の光学レンズや眼鏡レンズを被洗浄物とし、これらの表面に付着乃至固着している有機系異物(例えば大気中のこみに由来する汚染物や手指接触による汚染物等)を除去するためにも用いられる。

また紫外線照射条件は、被洗浄物の材質及び洗浄処理前に経てきた工程等により適宜決定しうる。

すなわち、紫外線を照射する光源として、水銀アークランプ、中圧水銀ランプ、高圧水銀ランプ、キセノンランプ、蛍光灯等を用いてもよく、また導入ガスとして、上の実施例で用いたウェットエアの代りにドライエアやオゾン(O₃)等を使用しても良く、さらにパワー、処理時間等も任意に変動させることができる。また酸素等のガスを含有する雰囲気中で紫外線を照射しても良く、この場合には酸素が紫外線照射時にオゾンになって、被洗浄物上に付着している汚れ成分の酸化分解等が促進される。またアルゴン、窒素等の不活性ガスを含有する雰囲気中で紫外線を照射しても良い。照射する紫外線の波長は上の実施例に記したものの以外に任意の波長であってよいが、有機物等の異物を効果的に減少・除去せしめるためには1000~3000Åの波長を有する紫外線を照射することが望ましい。

また上の実施例では、純水洗浄に先立って紫外線照射処理を行なったが、本発明の方法において、紫外線照射処理時間はこれに限定されるものでは

なく、脱脂洗浄後で純水洗浄前または純水洗浄後でIPA洗浄前に紫外線照射処理を実施しても良く、また例えば脱脂洗浄前及び脱脂洗浄後で純水洗浄前の如く紫外線照射処理を2回以上行なっても良い。

また上の実施例では、紫外線照射処理後の洗浄処理として、脱脂、純水、IPAによる順次洗浄処理を採用したが、本発明の方法において用いられる洗浄処理はこれに限定されるものではなく、例えば過酸化水素水のみ、IPAのみ、または過酸化水素とIPAを用いる洗浄処理を採用することができ、例えば過酸化水素水のみまたはIPAのみを用いる洗浄処理においては、過酸化水素水またはIPAによる洗浄前に被洗浄物の紫外線処理が行なわれ、また過酸化水素水とIPAを用いる洗浄処理では、過酸化水素水洗浄前、過酸化水素水洗浄後で純水洗浄前または純水洗浄後でIPA洗浄前の任意の段階に紫外線照射処理が行なわれる。

もちろん被洗浄物の洗浄液中への浸漬洗浄に際

して、洗浄液中に超音波を伝達させたり、あるいは被洗浄物を揺動させたりすることは任意である。

また洗浄処理として、上述の被洗浄物を洗浄液中に浸漬する方法の代りにスピンナー等で被洗浄物を回転させながら洗浄液をスプレーする方法や被洗浄物に加圧（高圧ジェット化）された洗浄液を噴きつける方法などを採用することもできる。

上の実施例では被洗浄物の乾燥処理として、IPA蒸気による熱気乾燥を採用したが、フロン等の他の蒸気を用いる蒸気乾燥でも良く、またスピン乾燥でも良い。

本発明の方法は、紫外線照射処理を行なわない通常の洗浄方法を突進した結果、異なる種類の洗浄液（例えば硫酸とアルコール）の化学反応による汚れが発生した被洗浄物の再洗浄のためにも有効であり、紫外線照射処理後に洗浄液による汚洗処理を行なうことによって、通常の条件では除去困難な汚れを除去することが可能である。

〔発明の効果〕

以上詳説したように、本発明の方法はフォトマ

スク、フォトマスクブランク、ガラス基板、半導体基板等、更には光学レンズや眼鏡レンズ等の硬表面を有する物品を効果的に洗浄化することを実現するものであり、その工業的価値は極めて多大である。

特許出願人 ホーヤ株式会社
代理人 弁護士 中 村 勝 男

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Inventor: Akinori Shindo

Applicant: Hoya Corporation

2-7-5 Nakaochiai, Shinjuku-ku, Tokyo

Agent: Patent Attorney Shizuo Nakamura

SPECIFICATION

1. Title of the Invention: METHOD FOR CLEANING HARD SURFACE

2. Claim

A method for cleaning a hard surface having organic foreign substances, comprising cleaning the hard surface with a cleaning solution, followed by drying, wherein a step of irradiating the hard surface with ultraviolet light is provided before any given step of cleaning with the cleaning solution.

3. Detailed Description of the Invention

[Industrial Field of the Invention]

The present invention relates to a method for cleaning a hard surface, and more particularly relates to a wet cleaning method which is used, for example, when a photomask blank, a photomask, a semiconductor substrate, or the like

is cleaned in a semiconductor process.

[Description of the Related Art]

The known wet cleaning method generally includes the steps of cleaning by immersing a workpiece to be cleaned in at least two cleaning solutions (e.g., sulfuric acid, pure water, and alcohol) one after another, and as required, by propagating ultrasonic waves into the cleaning solutions, and then drying by vaporizing the cleaning solutions by means of vapors of alcohol or the like.

[Problems to be Solved by the Invention]

However, when a workpiece is subjected to cleaning treatment by the wet cleaning method described above, the workpiece after cleaning is observed to have contamination in spite of the cleaning treatment. One of the reasons for this is that organic foreign substances such as a residual resist stuck on the workpiece are not completely removed by the cleaning treatment and partially remain on the workpiece after the cleaning treatment. Another reason is that organic foreign substances such as a residual resist stuck on the workpiece chemically react with a cleaning solution such as concentrated sulfuric acid, and a new reaction product is deposited on the surface of the workpiece. Still another reason is that different types of cleaning solutions used in the cleaning treatment chemically react with each other, and a new reaction product is generated on the

surface of the workpiece. The generation of contamination due to the chemical reaction between the different types of cleaning solutions will be further described in detail. In order to clean this type of workpiece, for example, cleaning treatment in which concentrated sulfuric acid immersion cleaning and alcohol immersion cleaning are combined is employed. In this cleaning treatment, after concentrated sulfuric acid immersion cleaning is performed in one vessel, pure water immersion cleaning is performed in three vessels before alcohol immersion cleaning in one vessel. Even if such pure water cleaning treatment is intervened, when foreign substances or the like exist on the surface of the workpiece or surface wettability of the workpiece is not uniform, sulfuric acid sticks and remains on the surface of the workpiece after pure water treatment and reacts with alcohol in the subsequent alcohol immersion cleaning treatment to generate a kind of esterified reaction product. In such a case, it is difficult to remove contamination due to the reaction product even by cleaning again with a cleaning solution such as sulfuric acid or alcohol, which is particularly troublesome.

As described above, in the known wet cleaning method, it is difficult to completely remove contamination due to organic foreign substances stuck on the workpiece, and new contamination may occur on the surface of the workpiece

because of a reaction between the organic foreign substances and a cleaning solution or a reaction between the individual cleaning solutions.

The present invention overcomes the foregoing problems. It is an object of the present invention to provide a method for cleaning in which contamination due to organic foreign substances stuck on the surface of a workpiece can be completely removed and new contamination associated with cleaning treatment can be prevented.

[Means for Solving the Problems]

The present invention was made to achieve the object described above, and in a method for cleaning a hard surface having organic foreign substances with a cleaning solution, followed by drying, a step of irradiating the hard surface with ultraviolet light is provided before any given step of cleaning with the cleaning solution.

[Operation]

By irradiating a workpiece with ultraviolet light before cleaning with a cleaning solution, organic foreign substances such as a photoresist that remain on the surface of the workpiece are subjected to a chemical reaction, and the organic foreign substances may be decomposed and disappear at that stage or may become to be easily dissolved or removed by a cleaning solution in the subsequent cleaning treatment with the cleaning solution. Therefore, the

organic foreign substances do not remain on the surface of the workpiece after the cleaning treatment with the cleaning solution.

Additionally, by the ultraviolet radiation treatment, since the organic foreign substances do not exist on the surface of the workpiece any more during cleaning treatment, a new reaction product is not generated due to a chemical reaction between the organic foreign substances and the cleaning solution.

Moreover, since surface wettability of the workpiece is improved by the ultraviolet radiation treatment, the cleaning solution spreads over the surface of the workpiece uniformly, and cleaning treatment with the cleaning solution can be performed uniformly over the entire workpiece, and also draining is easily performed when the workpiece is withdrawn from the cleaning solution and the cleaning solution does not remain partially concentrated on a portion of the surface of the workpiece. Thereby, for example, in a cleaning method in which sulfuric acid immersion cleaning treatment and alcohol immersion cleaning treatment are combined, if a simple pure water immersion cleaning treatment step for eliminating sulfuric acid that remains slightly on the surface of the workpiece is provided between the sulfuric acid treatment and the alcohol treatment, new contamination due to a chemical reaction between sulfuric

acid and alcohol do s not occur.

[Example]

With resp ct to a conventional m thod for cleaning a photomask in which a workpiece is subjected to sulfuric acid cleaning, pure water cleaning, and isopropyl alcohol (hereinafter abbreviated as IPA) cleaning in that order, followed by drying using IPA vapors, an example in which the workpiece is subjected to ultraviolet radiation treatment before sulfuric acid cleaning will be described below.

As a workpiece, a photomask obtained by the known steps of resist, etching, and photoresist stripping was used. That is, in order to obtain the photomask as a workpiece, AZ-1350 (manufactured by Hoechst) as a positive photoresist was applied on a photomask blank in which a chrome shading film was formed on a transparent glass substrate, exposure and development were performed through a mask having a predetermined pattern, the shading film was etched using the resist pattern as a mask, and then the resist pattern was stripped.

Four sheets of such a photomask with dimensions of 5 x 5 x 0.09 inch were placed in an ultraviolet irradiation system (treatment-chamber volume: 3,240 cm³) and ultraviolet radiation treatment was performed.

Treating conditions are as follows.

Ultraviolet source: low-pressure mercury-vapor lamp.

in which the intensity of an emission line at 2,537 Å occupies 90% and the intensity of an emission line at 1,849 Å occupies several percents of the total intensity.

Total power applied to low-pressure mercury-vapor lamp:
770 W

Wet air: Introduced at a velocity of 30 l/minute from a gas inlet of the ultraviolet irradiation system. Wet air improves the efficiency of O₃ generation during ultraviolet radiation.

Treating time: 5 minutes

After ultraviolet radiation treatment, the workpiece was subjected to cleaning treatment, followed by drying treatment. That is, cleaning treatment was performed by immersing the workpiece in one-vessel concentrated sulfuric acid having a concentration of 98% for 5 minutes, next by immersing in one-vessel pure water for 30 seconds, and further by immersing in one-vessel IPA for 3 minutes. With respect to the immersion of the workpiece in the IPA vessel, ultrasonic cleaning was performed by propagating ultrasonic waves into the IPA solution. (An ultrasonic oscillator for generating frequencies of 45 kHz and 46 kHz alternately was used. Applied power was 400 W.)

Drying treatment after the cleaning treatment was performed by exposing the workpiece withdrawn from the IPA

v ss l to IPA vapors.

With respect to 16 workpieces which were cleaned and dried after ultraviolet radiation treatment as described above, the cleanliness level was inspected. Contamination was not observed in all 16 workpieces.

With respect to 15 workpieces which were cleaned and dried in a similar manner without performing ultraviolet radiation treatment, the cleanliness level was inspected. Contamination was observed in the entire surfaces of all 15 workpieces. Even when pure water immersion cleaning treatment was performed in three vessels and the immersion time was set for 100 seconds each, contamination was often observed in the entire surface of the workpiece when ultraviolet radiation was not performed.

As a result of this example, in the method in which ultraviolet radiation treatment is performed in accordance with the present invention, organic foreign substances stuck on the workpieces are effectively removed and a new reaction product associated with a chemical reaction during cleaning treatment is not generated, and thereby it is clear that cleanliness of the workpieces after cleaning treatment can be secured satisfactorily.

Although in the example described above, a photomask stuck with a residual positive (photodegradable) photoresist was used, in the method in accordance with the present

invention, a workpiece stuck with a residual negative (photo-setting) photoresist may be cleaned, and in the case of positive and negative electron beam resists, the method also can be used similarly.

The method in accordance with the present invention is not limited to cleaning of photomasks. Photomask blanks, glass substrates, glass substrates provided with transparent conductive films, silicon wafers, and the like, and additionally, optical lenses such as camera lenses and spectacle lenses may be considered as workpieces, and the method is used to remove organic foreign substances (e.g., contaminants due to dust in air or contaminants due to finger contact) attached or stuck to the surfaces thereof.

Ultraviolet radiation conditions may be selected appropriately depending on materials of workpieces and processes undergone before cleaning treatment. That is, as a light source for ultraviolet radiation, a mercury arc lamp, a medium-pressure mercury lamp, a high-pressure mercury lamp, a xenon lamp, a heavy-water lamp, or the like may be used. As an induction gas, instead of wet air used in the example described above, dry air, ozone (O_3), or the like may be used. Moreover, power and treating time may be varied voluntarily. Ultraviolet radiation may be performed in an atmosphere containing a gas such as oxygen, and in such a case, oxygen changes into ozone during ultraviolet radiation

and oxidative destruction or the like of contaminants stuck on the workpiece is accelerated. Ultraviolet radiation may also be performed in an atmosphere containing an inert gas such as argon or nitrogen. Although ultraviolet light radiated may have a given wavelength in addition to that described in the example, in order to effectively reduce and remove foreign substances such as organic substances, it is desirable that ultraviolet light having a wavelength of 1,000 to 3,000 Å be radiated.

Although ultraviolet radiation treatment was performed before sulfuric acid cleaning in the example described above, the timing of ultraviolet radiation treatment is not limited to this in accordance with the method of the present invention. Ultraviolet radiation treatment may be performed after sulfuric acid cleaning and before pure water cleaning or after pure water cleaning and before IPA cleaning, or ultraviolet radiation treatment may be performed at least twice, for example, before sulfuric acid cleaning, and after sulfuric acid cleaning and before pure water cleaning.

With respect to cleaning treatment after ultraviolet radiation treatment, although sulfuric acid, pure water, and IPA were used in that order in the example described above, cleaning treatment used in the method of the present invention is not limited to this. For example, cleaning treatment using aqueous hydrogen peroxide only, IPA only, or

hydrogen peroxide and IPA may be adopted. In cleaning treatment using aqueous hydrogen peroxide only or IPA only, ultraviolet radiation treatment is performed before cleaning with aqueous hydrogen peroxide or IPA, and in cleaning treatment using aqueous hydrogen peroxide and IPA, ultraviolet radiation treatment is performed at a given stage before aqueous hydrogen peroxide cleaning, after aqueous hydrogen peroxide cleaning and before pure water cleaning, or after pure water cleaning and before IPA cleaning.

Of course, when a workpiece is subjected to immersion cleaning in a cleaning solution, ultrasonic waves may be propagated into the cleaning solution, or the workpiece may be oscillated.

As cleaning treatment, instead of immersing a workpiece in a cleaning solution as described above, a method of spraying a cleaning solution while a workpiece is rotated by a spinner or the like, or a method of spraying a workpiece with a pressurized (high-pressure jet) cleaning solution may be adopted.

With respect to drying treatment of the workpiece, although vapor drying by IPA vapors was adopted in the example described above, vapor drying using other vapors such as flon may be used, or spin drying may be used.

The method of the present invention is also effective

in r cl aning a workpi ce in which contamination has occurred due to a chemical reaction betw n diff r nt types of cleaning solutions (for xample, sulfuric acid and alcohol) as a result of carrying out a general cleaning process without ultraviolet radiation treatment. By recleaning treatment with a cleaning solution after ultraviolet radiation treatment, contamination that is not removable under normal conditions can be removed.

[Advantages]

As described above in detail, the method in accordance with the present invention makes it possible to effectively clean photomasks, photomask blanks, glass substrates, semiconductor substrates, and the like, and also articles having hard surfaces such as optical lenses and spectacle lenses, and the industrial significance of the invention is great.

Applicant for Patent	Hoya Corporation
Agent Patent Attorney	Shizuo Nakamura

